# Ultra Lightweight High Pressure Hydrogen Fuel Tanks Reinforced with Carbon Nanotubes

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Applied Nanotech, Inc. May 15, 2012

Project ID # ST105

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## **Overview**

## **Timeline**

• Project start date: Aug. 8, 2012

Project end date: Aug. 7, 2014

• Percent complete: 25-30%

## **Budget**

Total project funding

DOE share: \$999,990

Contractor share: 0

• Funding received in FY12: \$94,722

• Funding for FY13: \$499,995

## **Barriers**

- Barriers addressed
  - Cost of hydrogen storage tanks;
  - Weight of the storage tanks;
  - Performance of the storage tanks.
- Target
  - Reduce the cost of the hydrogen storage tanks by lowering their weight (>20%).

### **Partners**

- Lincoln Composites, Inc. (Subcontractor)
- Prof. Don Paul (University of Texas at Austin) -Consultant

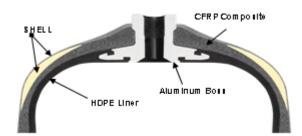


## Relevance

Our goal is to make the hydrogen storage tanks stronger, lighter and with better performance through CNT reinforced CFRP composites. As a result, the cost of the hydrogen storage tanks will be significantly reduced while increasing vehicle efficiency.

#### **DOE Barriers**

- Cost of hydrogen storage tanks
- Weight of the storage tanks
- Cost of the carbon fiber is too high



Cross-section view of a hydrogen storage tank (CFRP portion occupies 53wt.% of the tank)

| <b>Base Materials for CFRP</b> | Price (\$/kg) |
|--------------------------------|---------------|
| Neat Epoxy Resin               | 8.25          |
| Toray T700 Carbon Fiber        | 33            |
| CNT (1.0 wt.%) Epoxy Resin     | 11.17         |
| Neat Epoxy Resin + Carbon      | 25.58         |
| Fiber (Weight Ratio 3:7)       |               |
| CNT (1.0 wt.%) + Neat Epoxy    | 26.45         |
| Resin + Carbon Fiber           | (+3.4%)       |

| Hydrogen fuel tank<br>(Composite type IV,<br>5,000 psi) | Price of<br>Carbon<br>fiber (\$) | Price<br>of<br>Resin<br>(\$) | Labor &<br>Other<br>Costs (\$) | Cost of<br>CFRP<br>Portion<br>(\$) | Total Cost<br>of Tank<br>(\$) |
|---|----------------------------------|------------------------------|--------------------------------|------------------------------------|-------------------------------|
| Baseline  | 1224.3                           | 131.18                       | 755.52                         | 2111                               | 2727                          |
| 20% Weight  | 979.44                           | 142.08                       | 755.52                         | 1877.04                            | 2493.04                       |
| Reduction w/ CNTs                                       |                                  |                              |                                | (-11%)                             | (-9%)                         |
| 40% Weight  | 734.58                           | 106.56                       | 755.52                         | 1596.66                            | 2112.56                       |
| Reduction w/ CNTs                                       |                                  |                              |                                | (-24%)                             | (-23%)                        |

Based on our careful calculations, the cost for 1 kg of the CNT reinforced epoxy resin is the following based on high volume manufacturing:

Epoxy: \$8.25/kg

CNT: \$1 (\$0.1/g, 10 g will be used in the epoxy assuming 1% loading)

Production cost (including labor): \$2

So, the total cost for 1 kg of the CNT (1.0%) reinforced epoxy resin is \$11.17 ((0.99x8.25) + (0. 1x10) +2)) making the cost increase of 35% compared to the base epoxy (\$8.25/kg). It can be seen that the cost of the CFRP composite increases about 3.4% using 1% CNT reinforcement (including all related production costs of the reinforced epoxy resin). According to a 2010 TIAX report, carbon fiber reinforced polymer accounts for 77% of the total cost of a hydrogen fuel tank. Assuming a 5,000 psi tank, if we can lower the weight by 20% for the CFRP portion using CNT reinforcement, we are able to reduce the cost by at least 10% for the total tank. If we are able to lower the weight of the CFRP portion by 40%, the total cost for a tank can be further reduced by a total of nearly 23%.



# **Objectives**

| # | Objectives  |
|---|---|
| 1 | Demonstrate that we can further control NH <sub>2</sub> -functionalization level of the CNTs with the goal of further improving the mechanical properties of the epoxy matrix. We achieved this objective.  |
| 2 | Demonstrate that we can improve the strength by more than 60% and the modulus by more than 100% in the epoxy matrix by reinforcing it with NH <sub>2</sub> -functionalized CNTs and SiO <sub>2</sub> nanoparticles. This objective is over 90% completed.   |
| 3 | Demonstrate that the CNT reinforced epoxy resin can successfully penetrate and integrate with the carbon fibers during the filament winding portion of the hydrogen fuel tank fabrication process.  |
| 4 | Demonstrate that the 5,000 psi hydrogen fuel tanks with 40% weight reduction of the CFRP portion utilizing CNT reinforcement perform better than the standard tanks based on sophisticated testing including burst, drop/cycle/burst, impact, and gunfire.  |
| 5 | Demonstrate that the 10,000 psi hydrogen fuel tanks with 40% weight reduction of the CFRP portion utilizing CNT reinforcement perform better than the standard tanks based on sophisticated testing including burst, drop/cycle/burst, impact, and gunfire. |

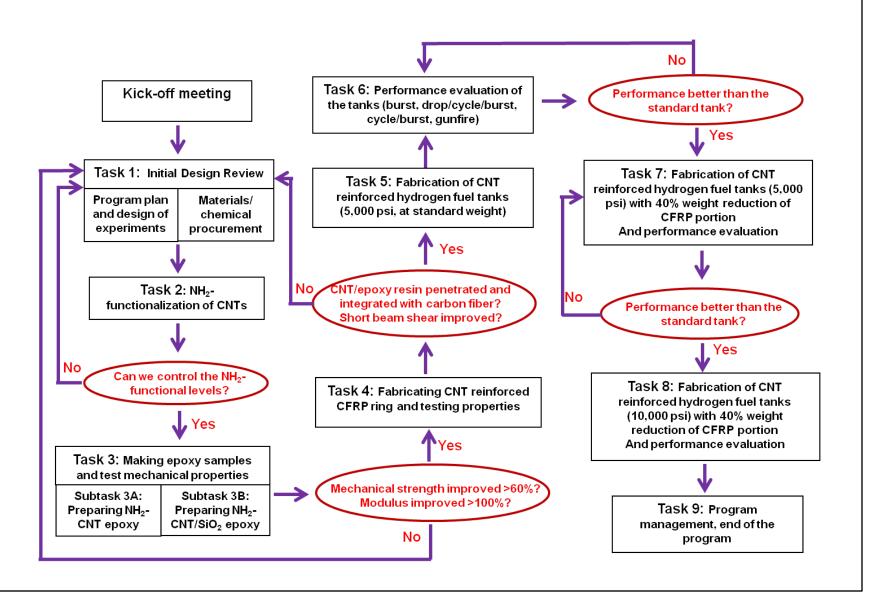


## **Approach**

Reducing the cost of high pressure hydrogen storage tanks - Our approach is to reduce the cost of the high pressure hydrogen storage tanks by lowering their weight. Using CNT reinforcement, we are able to significantly improve the mechanical properties of the carbon fiber/epoxy composite (CFRP) matrix used to construct the tanks with the final purpose being to lower the weight of the CFRP composites while preserving or even increasing the performance of the tanks.



## **Program Schedule**





# **Milestones**

| Milestone # | Progress Notes  | Timeline Start of month 1 |  |  |  |
|-------------|---|---------------------------|--|--|--|
| 1           | Kickoff Meeting   |                           |  |  |  |
| 2           | Initial design and material/chemical acquisition complete   | Month 1                   |  |  |  |
| 3           | NH <sub>2</sub> -functionalization of CNTs at different functional levels complete  | Month 4                   |  |  |  |
| 4           | Synthesis and mechanical evaluation of CNT/epoxy and CNT/SiO <sub>2</sub> /epoxy complete   | Month 6                   |  |  |  |
| 5           | 5 CNT reinforced CFRP ring made and tested, demonstrating that the CNT-reinforced epoxy can fully penetrate the carbon fibers                                   |                           |  |  |  |
| 6           | Fabrication of CNT reinforced hydrogen fuel tanks (5,000 psi) at standard weight complete   | End of Month 11           |  |  |  |
| 7           | Performance evaluation of the tanks complete  | Month 13                  |  |  |  |
| 8           | Fabrication of CNT reinforced hydrogen fuel tanks (5,000 psi) with 40% weight reduction of the CFRP portion complete. Better performance of the tanks achieve   | Month 18                  |  |  |  |
| 9           | Fabrication of CNT reinforced hydrogen fuel tanks (10,000 psi) with 40% weight reduction of the CFRP portion complete. Better performance of the tanks achieved |                           |  |  |  |
| 10          | Final Report Complete - Phase II program completion.  | Month 24                  |  |  |  |



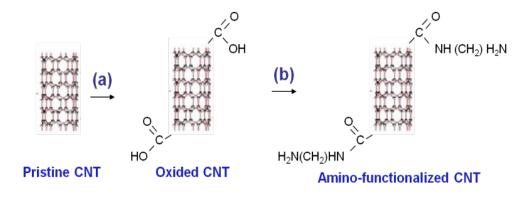
# Work Plan/Progress (for the First Year of the Program)

| Task | Task Description   | Progress/Accomplishments   | completion |  |
|------|--|--|------------|--|
|      | Kick-off meeting   | Dr. Dongsheng Mao of ANI attended the kick-off meeting organized by the DOE in September, 2012. He also attended the PI/Contractor meeting in Nov. 2012.   |            |  |
| 1    | Initial design review  |  |            |  |
|      | A - Design review  | ANI team had a number of meetings at the beginning of the program to discuss the design of experimentation and overall schedule. We also discussed with the subcontractor related to the Statement of Work | 100%       |  |
|      | B – Obtain materials and chemicals   | All the chemicals and materials were obtained in Sept. 2012 for the 1 <sup>st</sup> year of the program  | 100%       |  |
| 2    | Functionalization of CNTs at different levels  | We have prepared enough functionalized CNTs for the next task.   | 100%       |  |
| 3    | Synthesize epoxy samples reinforced with CNTs and SiO <sub>2</sub> nanoparticles   | We obtained further improved mechanical properties compared with the achievement obtained in the Phase I program   | 100%       |  |
| 4    | Fabricate CNT CFRP ring and test properties  We have already prepared 2 formulations of the CNT and SiO <sub>2</sub> reinforced epoxy resin. Lincoln Composites is working on fabrication of the CFRP rings at this stage. This task will be finished in early May, 2013. This task is going ahead as planned. |  | 30%        |  |
| 5    | Fabricate CNT reinforced tanks (5,000 In this task, we will produce large quantity of the CNT/epoxy resin, fabricate tanks, and test preliminary performance of the tanks. This task is going ahead as planned.  |  |            |  |
| 6    | Performance evaluation of tanks In this task, burst, drop/cycle/burst, gunfire, and impact properties of the tanks will be performed. This task is going ahead as planned. Portion of this task will be performed at the beginning of the 2 <sup>nd</sup> year.  |  |            |  |



## **Accomplishment and Progress - 1**

We were able to control the  $NH_2$ -functionalization of the CNTs which can significantly improve the mechanical properties of the epoxy resin used to fabrication hydrogen storage tanks.

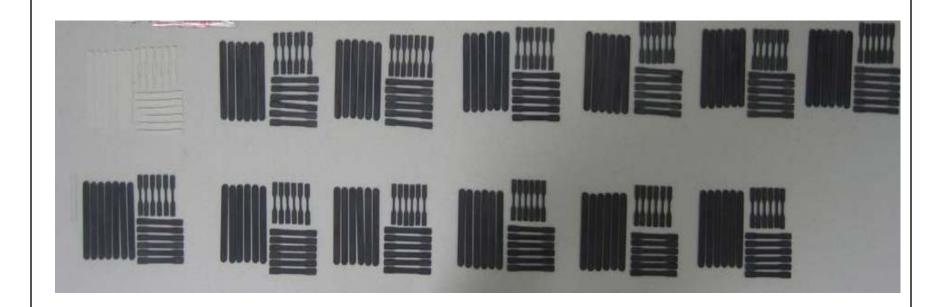


The  $\mathrm{NH_2}$ -functionalization process is a wet chemical process. During the functionalization, CNTs can be damaged although on the other hand they can be attached with functional groups. It is essential to find an optimized process that can significantly improve the mechanical properties of the epoxy matrix based on  $\mathrm{NH_2}$ -functionalization.



# **Accomplishment and Progress – 2**

A series of samples were made and tested based on CNT and  $SiO_2$  reinforced epoxy. Based on the results, we have determined the optimized  $NH_2$ -functionalization level and loading of the CNTs and  $SiO_2$  in the epoxy matrix.





# **Accomplishment and Progress - 3**

We were able to achieve further improved mechanical properties of the epoxy matrix based on  $NH_2$ -functionalized CNTs at optimized functionalization levels. At CNT loading of 1 wt.% (treatment for 2 hours), we were able to achieve significantly improved mechanical properties.

| Sample #   | NH <sub>2</sub> (2 hr) | NH <sub>2</sub> (4 hr) | NH <sub>2</sub> (8 hr) | NH <sub>2</sub> (16 hr) | Tensile  | Tensile | Flexural | Flexural | Compressio | Compression |
|------------|------------------------|------------------------|------------------------|-------------------------|----------|---------|----------|----------|------------|-------------|
|            | (%)                    | (%)                    | (%)                    | (%)                     | strength | modulus | strength | modulus  | n strength | n modulus   |
|            |                        |                        |                        |                         | (MPa)    | (GPa)   | (MPa)    | (GPa)    | (MPa)      | (GPa)       |
| Neat epoxy |                        |                        |                        |                         | 76.7     | 3.35    | 106.0    | 2.54     | 102.3      | 2.62        |
| 1          | 0.25                   |                        |                        |                         | 88.7     | 3.45    | 115.3    | 2.70     | 113.8      | 2.98        |
| 2          | 0.5                    |                        |                        |                         | 93.3     | 3.70    | 127.4    | 3.88     | 135.3      | 3.12        |
| 3          | 1                      |                        |                        |                         | 105.8    | 3.88    | 148.7    | 3.03     | 147.7      | 3.28        |
|            |                        |                        |                        |                         | (38%1)   | (16%↑)  | (40%↑)   | (19%↑)   | (44%↑)     | (25%↑)      |
| 4          | 2                      |                        |                        |                         | 90.1     | 4.01    | 129.3    | 4.25     | 140.3      | 3.97        |
| 5          | 3                      |                        |                        |                         | 80.4     | 4.08    | 117.1    | 4.58     | 135.4      | 4.18        |
|            |                        | 0.5                    |                        |                         | 87.0     | 3.62    | 117.1    | 2.68     | 115.8      | 3.47        |
|            |                        | 1                      |                        |                         | 96.6     | 3.78    | 128.6    | 3.07     | 157.0      | 4.28        |
|            |                        | 2                      |                        |                         | 89.3     | 3.87    | 135.7    | 3.08     | 133.3      | 4.50        |
|            |                        | 3                      |                        |                         | 83.8     | 3.80    | 113.7    | 2.69     | 134.6      | 4.57        |
| 6          |                        |                        | 0.25                   |                         | 80.7     | 3.53    | 110.0    | 2.67     | 117.8      | 3.01        |
| 7          |                        |                        | 0.5                    |                         | 87.2     | 3.68    | 120.0    | 2.67     | 117.8      | 3.51        |
| 8          |                        |                        | 1                      |                         | 95.6     | 3.88    | 124.3    | 2.98     | 133.4      | 4.01        |
| 9          |                        |                        | 2                      |                         | 80.1     | 3.99    | 116.0    | 3.28     | 127.3      | 4.50        |
| 10         |                        |                        | 3                      |                         | 78.0     | 4.23    | 107.9    | 3.30     | 129.5      | 4.37        |
|            |                        |                        |                        | 0.5                     | 76.0     | 3.13    | 116.3    | 3.03     | 118.3      | 2.68        |
| _          |                        |                        |                        | 1                       | 77.1     | 3.30    | 113.2    | 2.84     | 114.5      | 2.78        |
|            |                        |                        |                        | 2                       | 76.3     | 3.16    | 111.2    | 2.87     | 108.0      | 2.87        |
|            |                        |                        |                        | 3                       | 77.1     | 3.24    | 113.4    | 2.85     | 106.6      | 2.87        |



# **Accomplishment and Progress - 4**

 $NH_2$ -CNT and  $SiO_2$  co-reinforced epoxy samples were synthesized and characterized. We were able to achieve further improved mechanical properties. We already prepared and sent to Lincoln Composites, Inc. quantity of the samples 1 and 3 for CFRP ring fabrication and evaluation.

| Sample #   | NH <sub>2</sub> (2 hr)<br>(%) | SiO <sub>2</sub><br>(%) | Tensile<br>strength (MPa)    | Tensile<br>modulus<br>(GPa) | Flexural<br>strength<br>(MPa) | Flexural<br>modulus<br>(GPa) | Compression strength (MPa) | Compression modulus (GPa)   |
|------------|-------------------------------|-------------------------|------------------------------|-----------------------------|-------------------------------|------------------------------|----------------------------|-----------------------------|
| Neat epoxy | 0                             | 0                       | 76.7                         | 3.35                        | 106.0                         | 2.54                         | 102.3                      | 2.62                        |
| 1          | 0.25                          | 2.5                     | 92.3<br>(20% <sup>†</sup> )  | 3.74<br>(12%↑)              | 118.7<br>(12%↑)               | 2.97<br>(12% <sup>†</sup> )  | 121.8<br>(19%↑)            | 3.18<br>(21% <sup>†</sup> ) |
| 2          | 0.5                           | 2.5                     | 100.8                        | 4.04                        | 134.0                         | 3.31                         | 150.3                      | 3.41                        |
| 3          | 1                             | 2.5                     | 113.7<br>(48% <sup>†</sup> ) | 4.31<br>(28% <sup>†</sup> ) | 150.0<br>(41%↑)               | 3.48<br>(37%↑)               | 163.7<br>(60%↑)            | 4.13<br>(58%↑)              |
| 4          | 2                             | 2.5                     | 87.3                         | 4.28                        | 132.3                         | 3.38                         | 155.3                      | 3.93                        |
| 5          | 3                             | 2.5                     | 83.5                         | 4.14                        | 125.1                         | 3.50                         | 133.0                      | 3.90                        |
| 6          | 0.25                          | 5                       | 92.5                         | 3.80                        | 118.0                         | 3.05                         | 120.8                      | 3.14                        |
| 7          | 0.5                           | 5                       | 97.8                         | 4.01                        | 123.8                         | 3.40                         | 131.8                      | 3.55                        |
| 8          | 1                             | 5                       | 101.5                        | 4.11                        | 117.7                         | 3.40                         | 123.0                      | 3.67                        |
| 9          | 2                             | 5                       | 90.5                         | 4.30                        | 103.7                         | 3.48                         | 124.0                      | 3.78                        |
| 10         | 3                             | 5                       | 76.7                         | 4.38                        | 95.6                          | 3.60                         | 101.8                      | 3.70                        |
| 11         | 0.25                          | 12                      | 80.4                         | 4.01                        | 112.6                         | 3.00                         | 119.3                      | 3.04                        |
| 12         | 0.5                           | 12                      | 78.5                         | 4.12                        | 115.7                         | 3.08                         | 125.8                      | 3.38                        |
| 13         | 1                             | 12                      | 70.3                         | 4.34                        | 107.4                         | 3.35                         | 130.4                      | 3.59                        |
| 14         | 2                             | 12                      | 68.8                         | 4.40                        | 99.8                          | 3.77                         | 107.7                      | 3.53                        |
| 15         | 3                             | 12                      | 63.3                         | 4.58                        | 87.7                          | 3.60                         | 90.5                       | 3.48                        |



## **Next Key Task**



**CFRP** ring

- ❖ Modify fabrication process to allow CNT reinforced epoxy resins to fully penetrate and integrate with the carbon fiber during the filament winding process
- **❖**Solve viscosity issue to ensure the mechanical property improvement can be fully transferred to the CNT reinforced CFRP composite
  - ❖ Select optimal temperature to fabricate the rings by viscosity change vs. temp increase. The short beam shear of the rings will be tested.
  - Use a surfactant to decrease the loading of the CNT reinforced epoxy matrix

## **Collaboration**

#### **Subcontractor: Lincoln Composites**

Lincoln Composites, manufacturer of the TITAN™ and TUFFSHELL® tanks, is the leading provider of natural gas and hydrogen storage and transport solutions to the alternative fuel vehicle industry.

#### **Lincoln Composites' efforts in the 1st year of this Phase II Program:**

- ❖ Initial Design Review;
- \* Fabricate CNT reinforced CFRP rings and test properties (shear, impact, burst);
- ❖ Fabricate 3 baseline tanks, 3 tanks with CNT reinforcement, 3 tanks with CNT reinforcement at reduced weight and evaluate performance.



## **Future Work**

- Optimize the formulation of the functionalized CNT and SiO<sub>2</sub> co-reinforced epoxy based upon the result achieved so far..
- \* Improve the processing for fabricating hydrogen storage tanks using CNT reinforced epoxy that wasn't solved in the Phase I Program because of the viscosity issue.
- **❖** Continue to focus on the 5,000 psi pressure hydrogen storage tanks initially before moving to higher pressure tanks (for example 10,000 psi tanks)
- ❖ Evaluate the performance of the hydrogen fuel tanks (burst, cycle/burst, drop/cycle/burst, and gunfire, etc.)
- **♦ Move to higher pressure hydrogen storage tanks (10,000 psi at reduced weight)**
- Manufacturing

The goal of the fourth task will be to establish manufacturing protocols for the ultra light weight hydrogen high pressure fuel tanks demonstrated in the Phase II program.



# **Summary Slide**

# **Project Summary**

Relevance: Our purpose is to make the hydrogen storage tanks stronger, lighter and with better performance through CNT reinforced CFRP composite. As a result, the cost of the hydrogen storage tanks will be significantly reduced while increasing vehicle efficiency.

Approach: Reducing the cost of high pressure hydrogen storage tanks - Our approach is to reduce the cost of the high pressure hydrogen storage tanks by lowering their weight. Using CNT reinforcement, we are able to significantly improve the mechanical properties of the carbon fiber/epoxy composite (CFRP) matrix used to construct the tanks with the final purpose being to lower the weight of the CFRP composites while preserving or even increasing the performance of the tanks.

Technical Accomplishments and Progress: We were able to control the  $NH_2$ -functionalization level of the CNTs to significantly improve the mechanical properties of epoxy. We were able to achieve more than 60% improvement in the epoxy matrix of the compression strength and 60% improvement of the compression modulus based on CNT and  $SiO_2$  co-reinforcement. Tensile and flexural properties were also significantly improved (over 40%).

Proposed Future Research: We need to modify the filament winding process to fabricate high quality hydrogen storage tanks with CNT reinforced epoxy due to its higher viscosity compared with the control epoxy. We will continue to improve the mechanical properties of the epoxy matrix using functionalized CNTs; optimize the fabrication process of the hydrogen storage tanks; test the performance of the tanks with CNT reinforcement in more sophisticated ways; Based on the current result we achieved, we firmly believe we are able to achieve improved results in the Phase II program.

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